



PROMETH₂O

20IND06 PROMETH2O

WP1: Improved trace water measurement methods and techniques

Task 1.1: Development and improvement of optical analyzers



The EMPIR initiative is co-funded by the European Union's Horizon 2020 research and innovation programme and the EMPIR Participating States

❖ *To develop new and improved optical methods and techniques for trace water measurements*

Target: H₂O traces in Ar, N₂, H₂ [from 5 ppm (-65 °C) to 5 ppb (-105 °C) @ 0.1 MPa]. Relative uncertainty for the measurements: 3 % (5ppm) and 8 % (5 ppb)

4x systems:

- Enhancements in NIR comb-calibrated frequency-stabilized cavity ring down spectrometer (CC-FS-CRDS);
- NIR cavity-enhanced frequency modulated (CE-FM) spectroscopy hygrometer development;
- Far-UV absorption spectroscopy system development;
- Upgrade of existing high-resolution FTIR system.

4 partners:

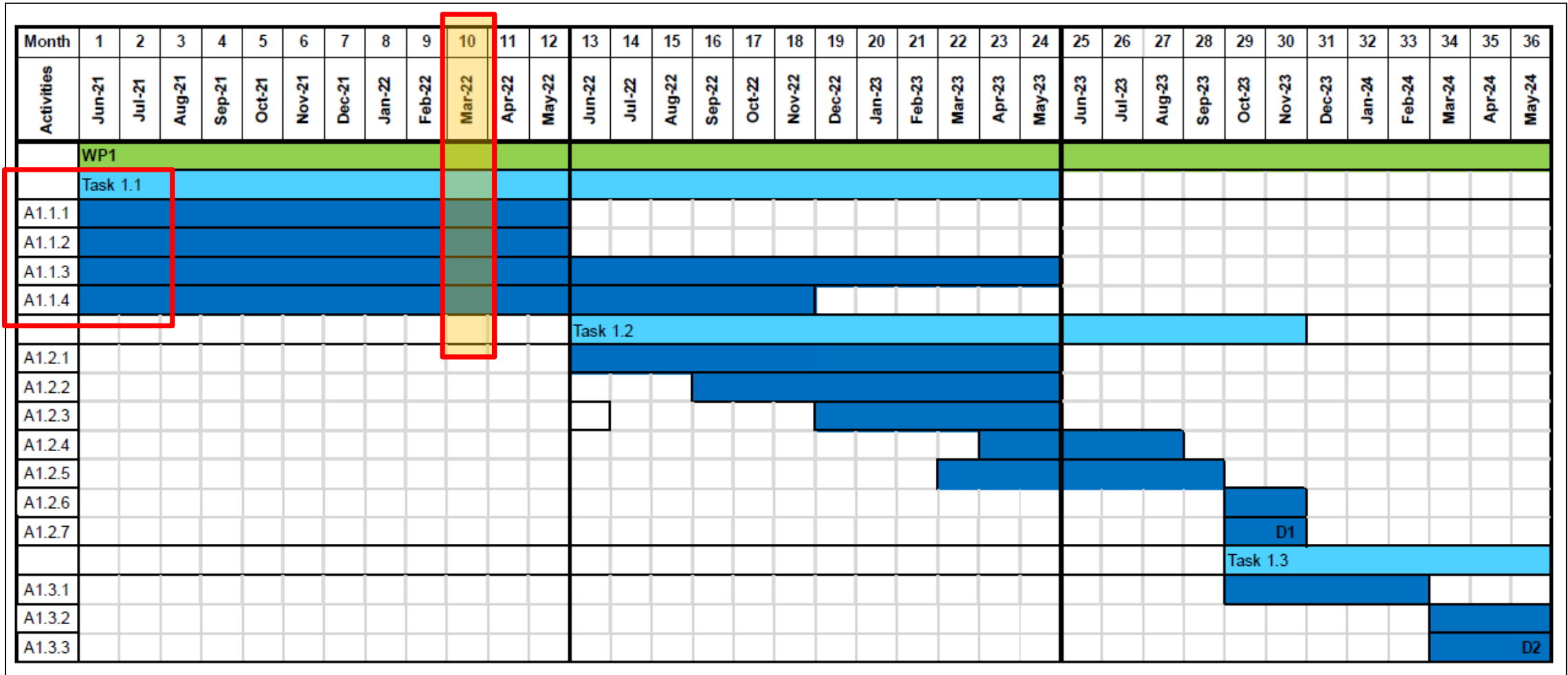
1x NMI, 2x UNI and 1x Company

Across the EUROPE:

- TUBITAK (TR)
- SUN (IT)
- DTU (DK)
- QROMETRIC (UK)

 **4x Activities**






A.1.1.1

CC-FS-CRDS for ultra-sensitive traceable
measurements of water vapor in UHP gases

By Antonio Castrillo

<p>A1.1.1 M12</p>	<p>Development of a compact CC-FS-CRDS spectrometer, referenced to an optical frequency comb, for traceable measurements of water vapour in H₂ and N₂ from 5 ppm down to 50 ppb with standard relative uncertainty between 3% and 8% and operation pressure as low as 10kPa.</p>	<p>SUN</p>
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Dual-laser frequency-stabilized cavity ring-down spectroscopy for water vapor density measurements

Eugenio Fasci¹, Hemanth Dinesan¹, Luigi Moretti¹ , Andrea Merlone², Antonio Castrillo¹  and Livio Gianfrani¹ 

Main features:

$$\tau \approx 75 \mu\text{s}; \quad \frac{\sigma_{\tau}}{\tau} = 0.56\%$$

$$\alpha_{min} = 5 \times 10^{-11} \text{ cm}^{-1}$$

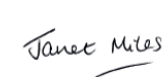
$$NEA = 6 \times 10^{-10} \frac{\text{cm}^{-1}}{\sqrt{\text{Hz}}}$$

Metrologia

This is to certify that the article

Dual-laser frequency-stabilized cavity ring-down spectroscopy for water vapor density measurements
by Eugenio Fasci, Hemanth Dinesan, Luigi Moretti, Andrea Merlone, Antonio Castrillo and Livio Gianfrani
Eugenio Fasci et al 2018 Metrologia 55 662

has been selected for inclusion in the
'Highlights of 2018' collection.

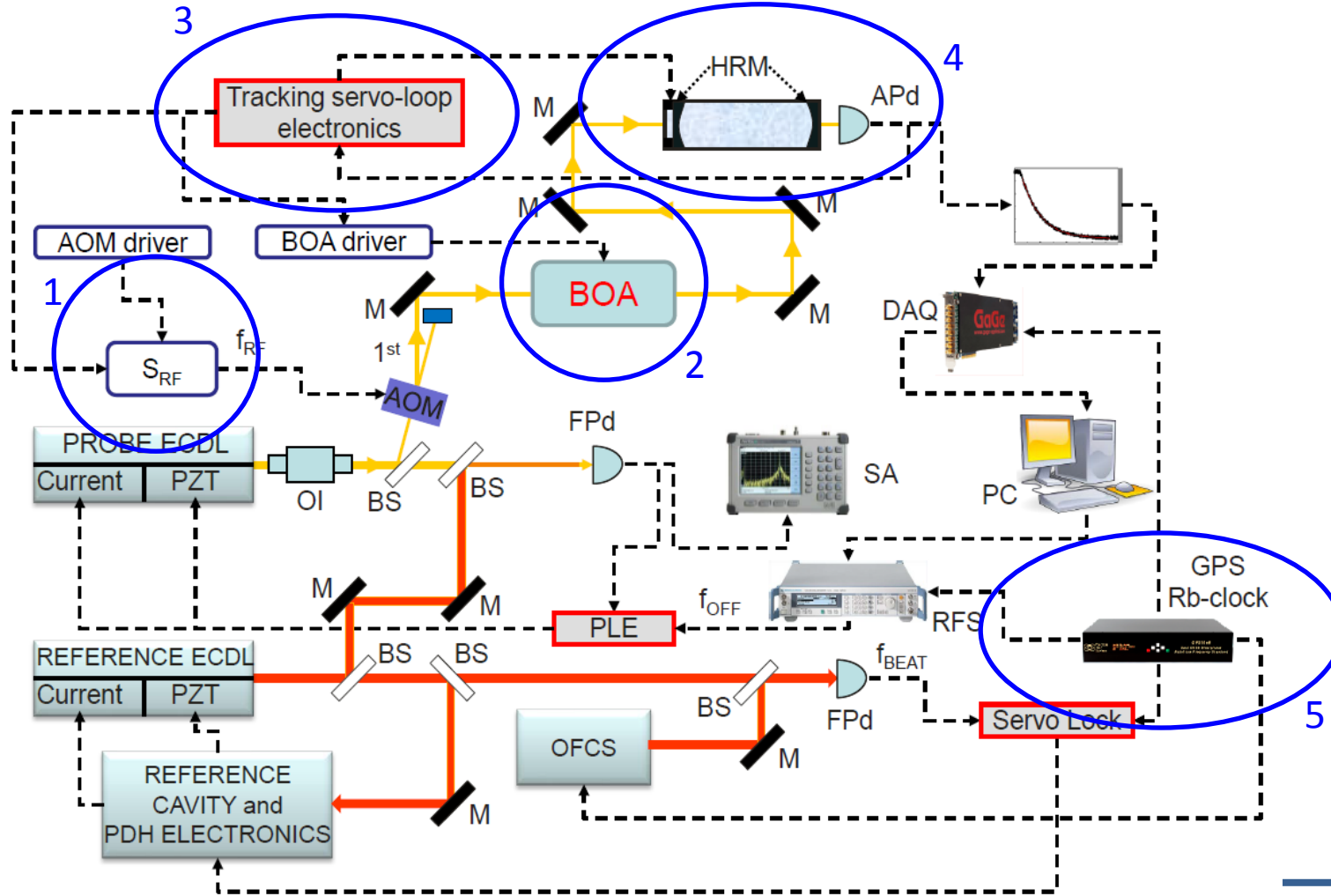


Janet Miles
Editor
Metrologia
iopscience.org/met



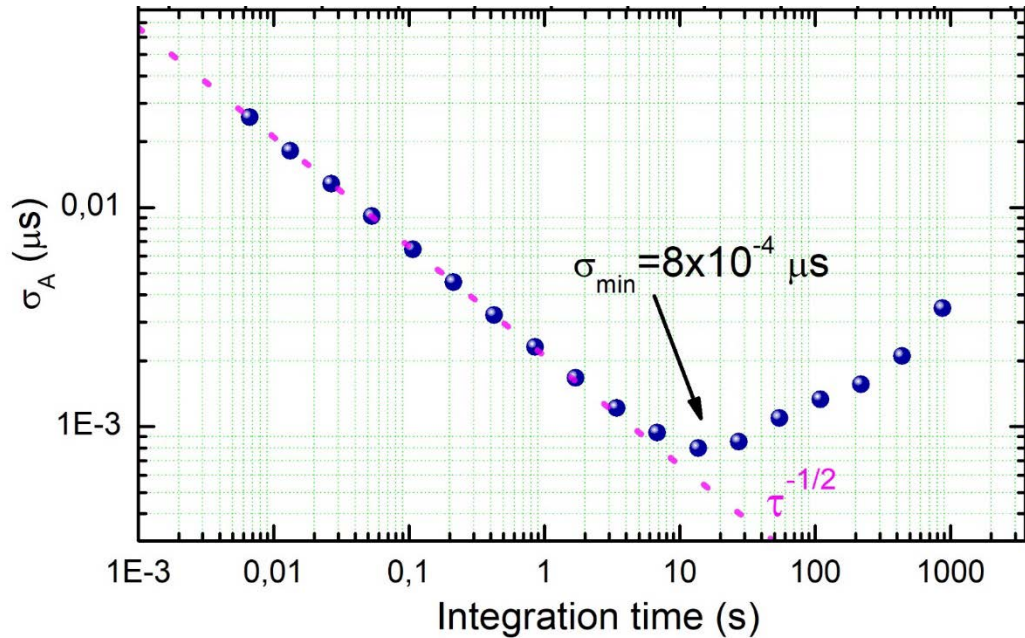
Ian Forbes
Publisher
Metrologia
iopscience.org/met


Improvements to the existing spectrometer



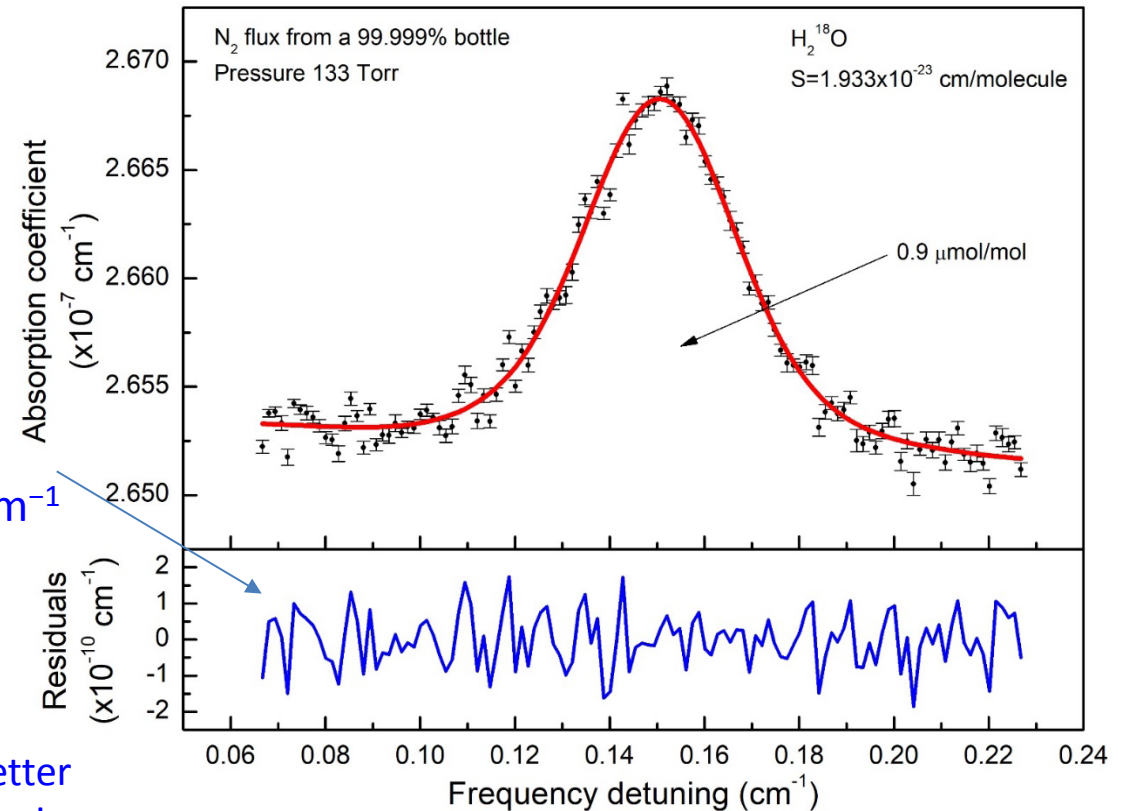
- 1) New RF switch: extinction ratio up to 90 dB;
- 2) Booster Optical Amplifier (BOA): input power enhanced up to 20 mW;
- 3) New tracking electronics: more compact;
- 4) New HR mirrors: ring down time up to 130 μ s;
- 5) New frequency chain: GPS disciplined.

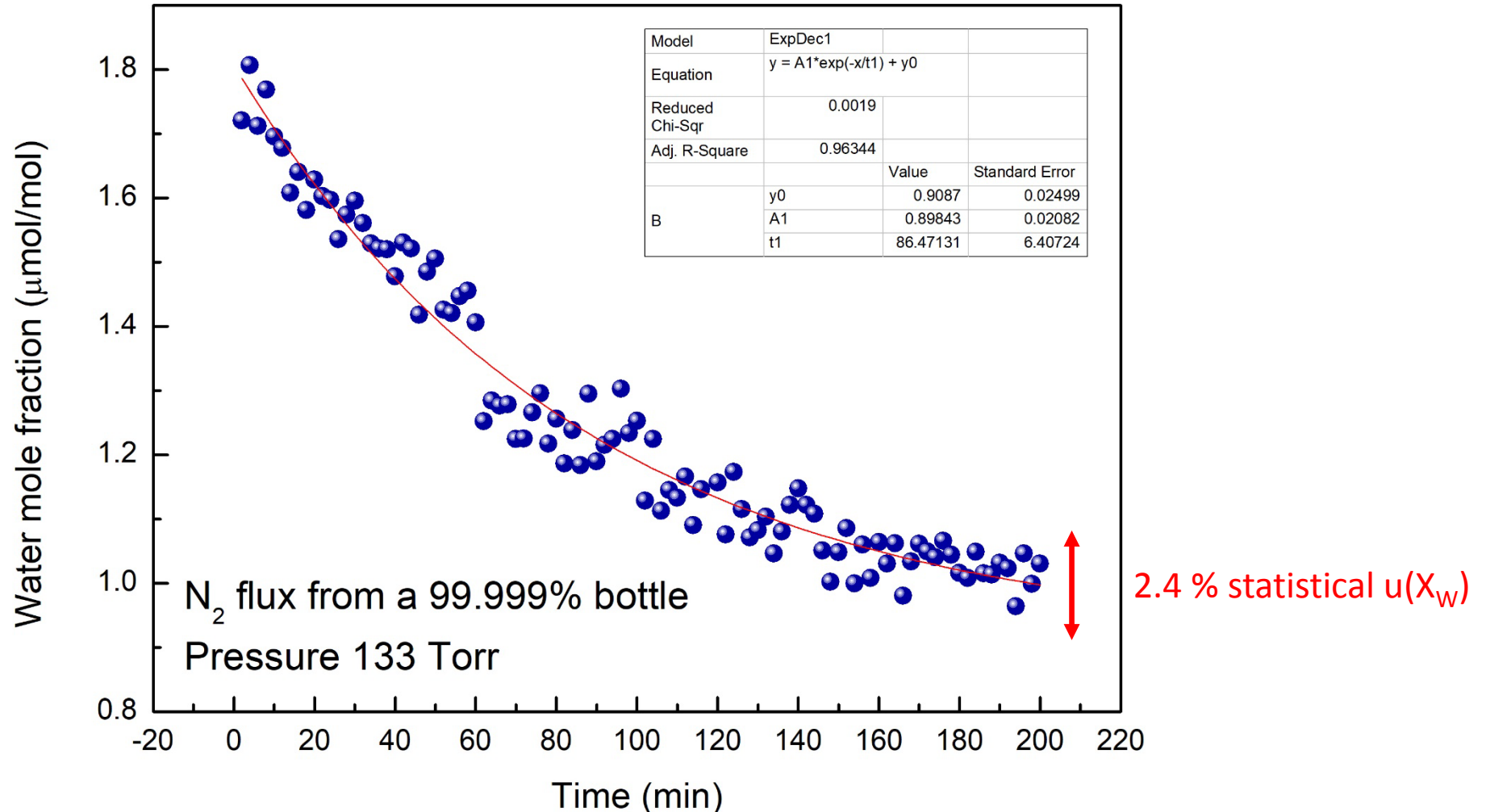
Present performance: $\tau \approx 130 \mu\text{s}$; $\frac{\sigma_\tau}{\tau} = 0.05\%$
 $\alpha_{min} = 9 \times 10^{-12} \text{ cm}^{-1}$
 $NEA = 3 \times 10^{-11} \frac{\text{cm}^{-1}}{\sqrt{\text{Hz}}}$



r.m.s.
 $7 \times 10^{-11} \text{ cm}^{-1}$

10 times better than before!

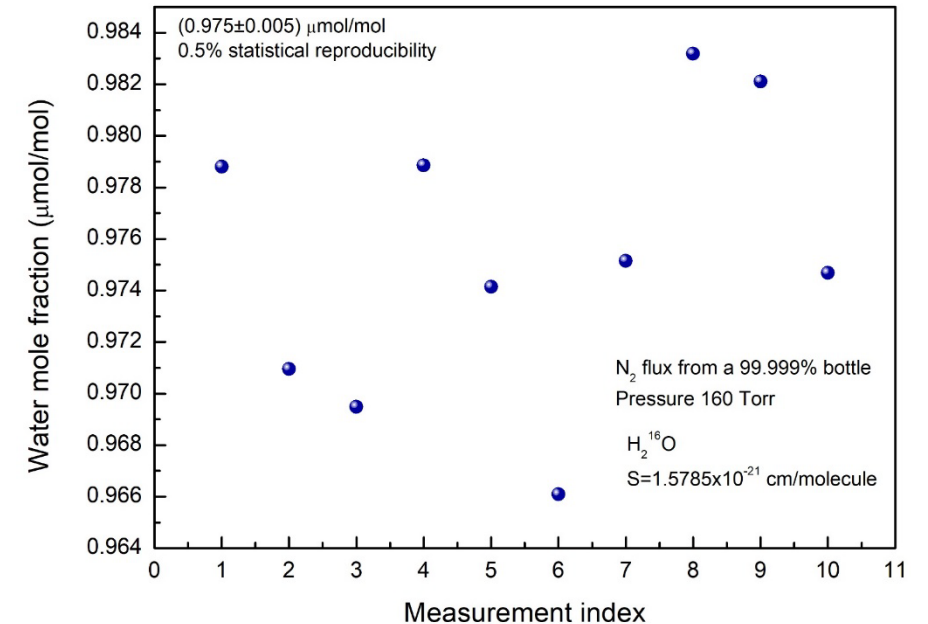
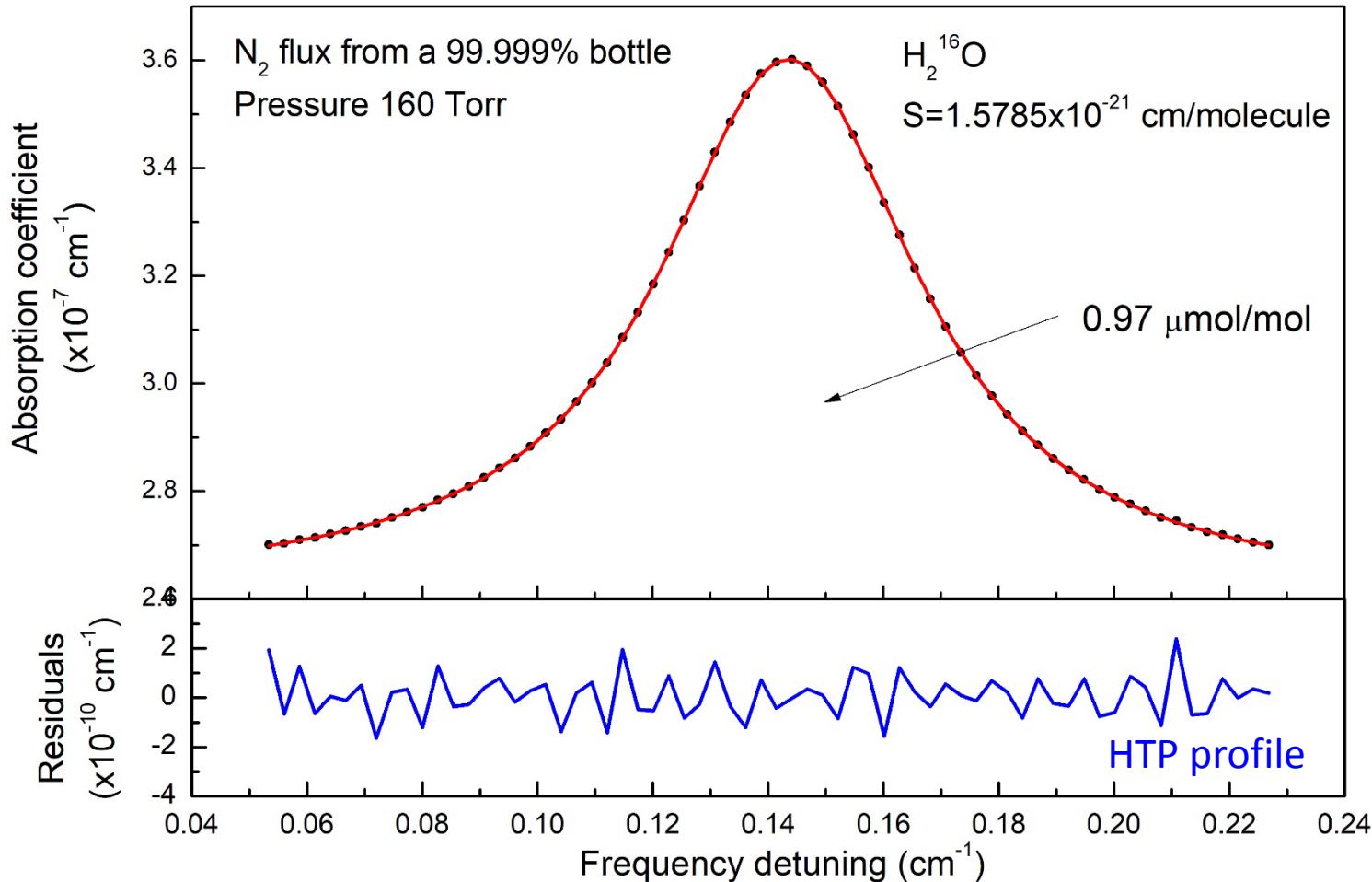
Detection of H_2^{18}O in 1 ppm of water in N_2





Line intensity (S) from PRA **79**, 052507 (2009)
 Measured @ NIST by J. Hodges *et al.* using a CRDS
 spectrometer and a primary standard humidity
 generator.

SI traceable uncertainty of 0.3% for S
Statistical uncertainty of 0.5% @ 1 ppm



$$X_w = \frac{\alpha_{TOT} k_B T}{S(T)P}$$

Contribution	Type A	Type B
(k=1)	(%)	(%)
Statistical	0.5 - 3	
Line strength		0.3
Frequency scale		Negligible
Line shape model		0.1
Gas temperature		0.05
Partition function		0.04
Pressure		0.1
Overall combined uncertainty	0.5 – 3.1 %	

- ✓ Make the spectrometer more compact (with minimization of absorption from water in air) using fiber optics components;
- ✓ New mirrors (from Five Nine) having higher reflectivity (i.e. further enhancement of the sensitivity);
- ✓ A new cavity spacer (electrically polished stainless steel);
- ✓ Selection of a stronger H₂¹⁶O transition @ 7181.15578 cm⁻¹ (S=1.5048x10⁻²⁰, SI uncertainty 0.3%);
- ✓ Simplify the laser frequency reference strategy;
- ✓ Comparison with a Tiger Optics instrument.

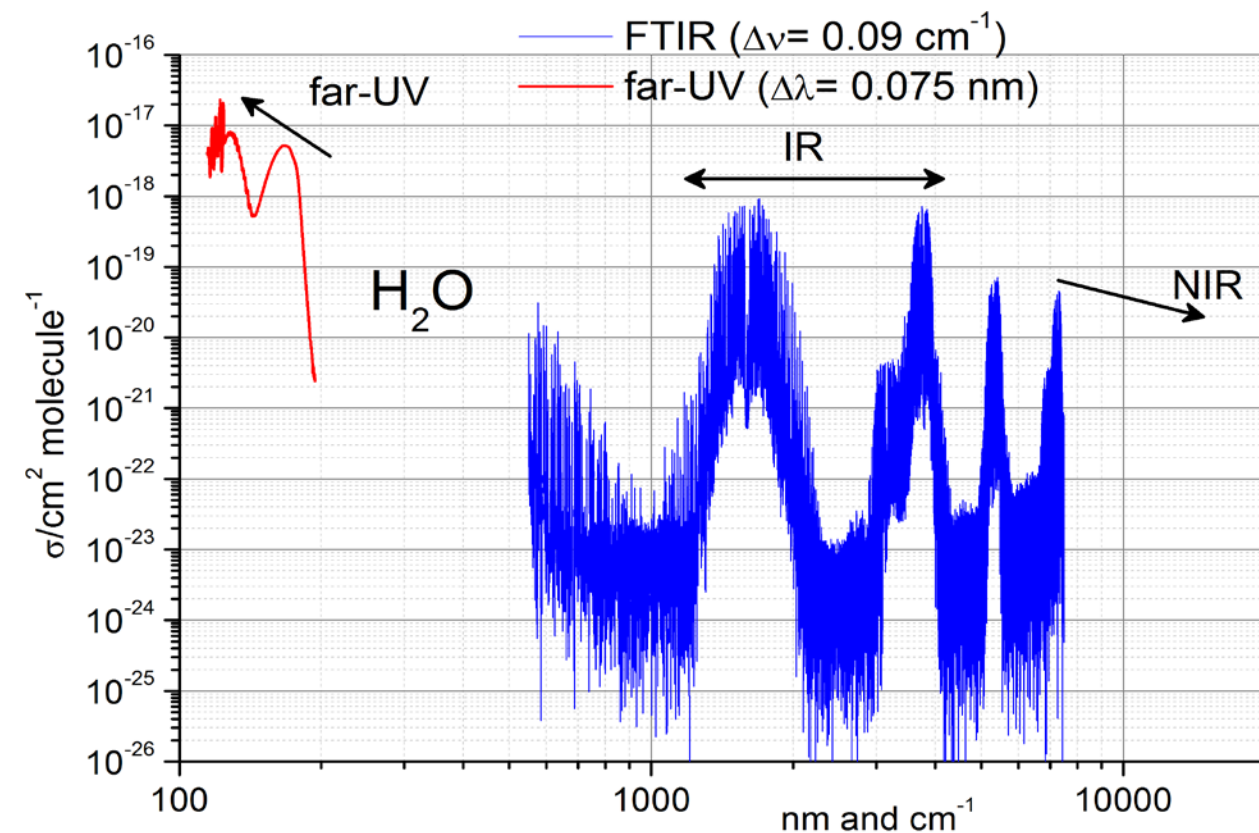


A.1.1.2

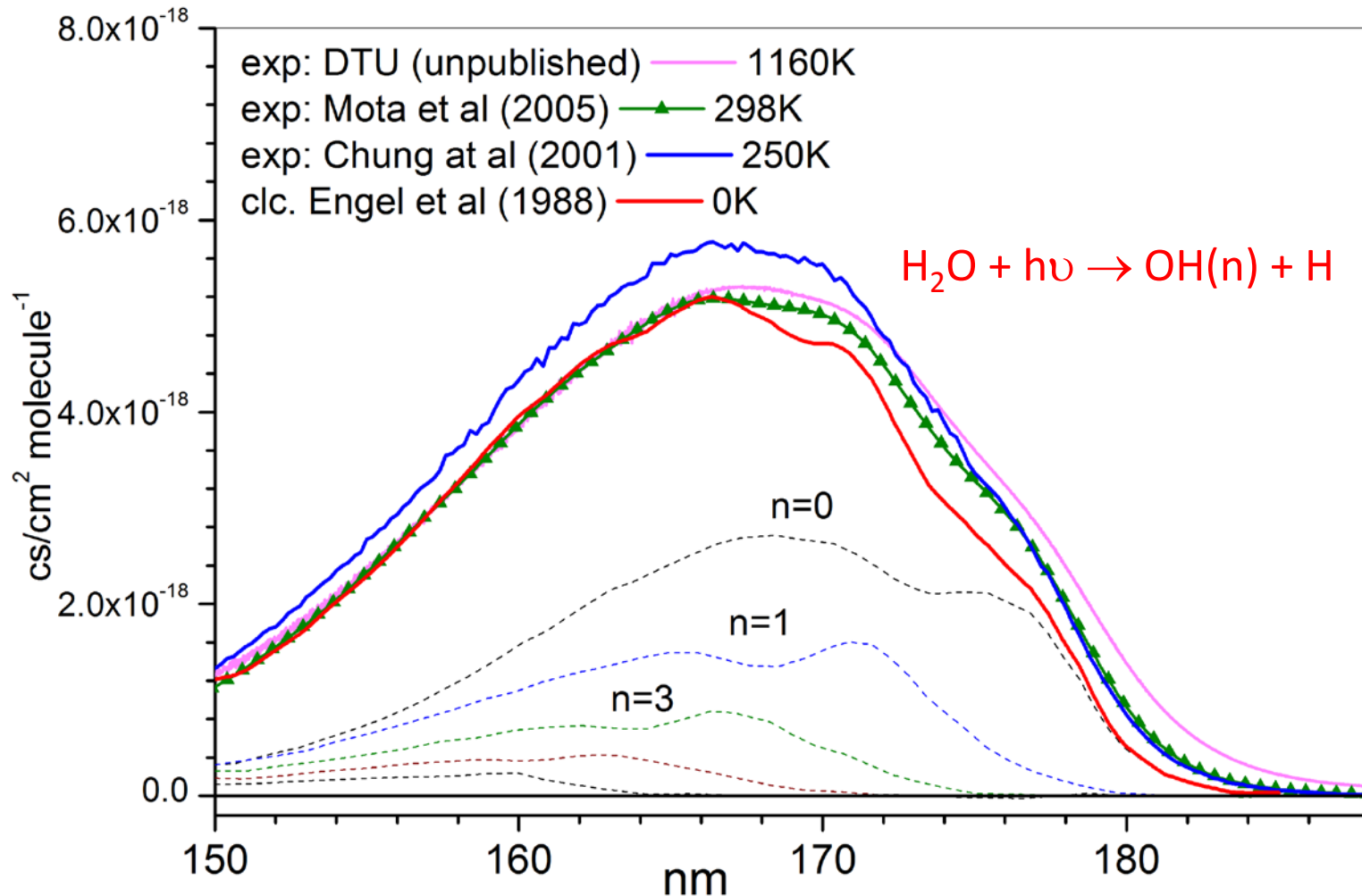
Develop a compact and transportable **far-UV** system

By Alexander Fateev

Large H₂O absorption cross sections in far-UV (< 200 nm)

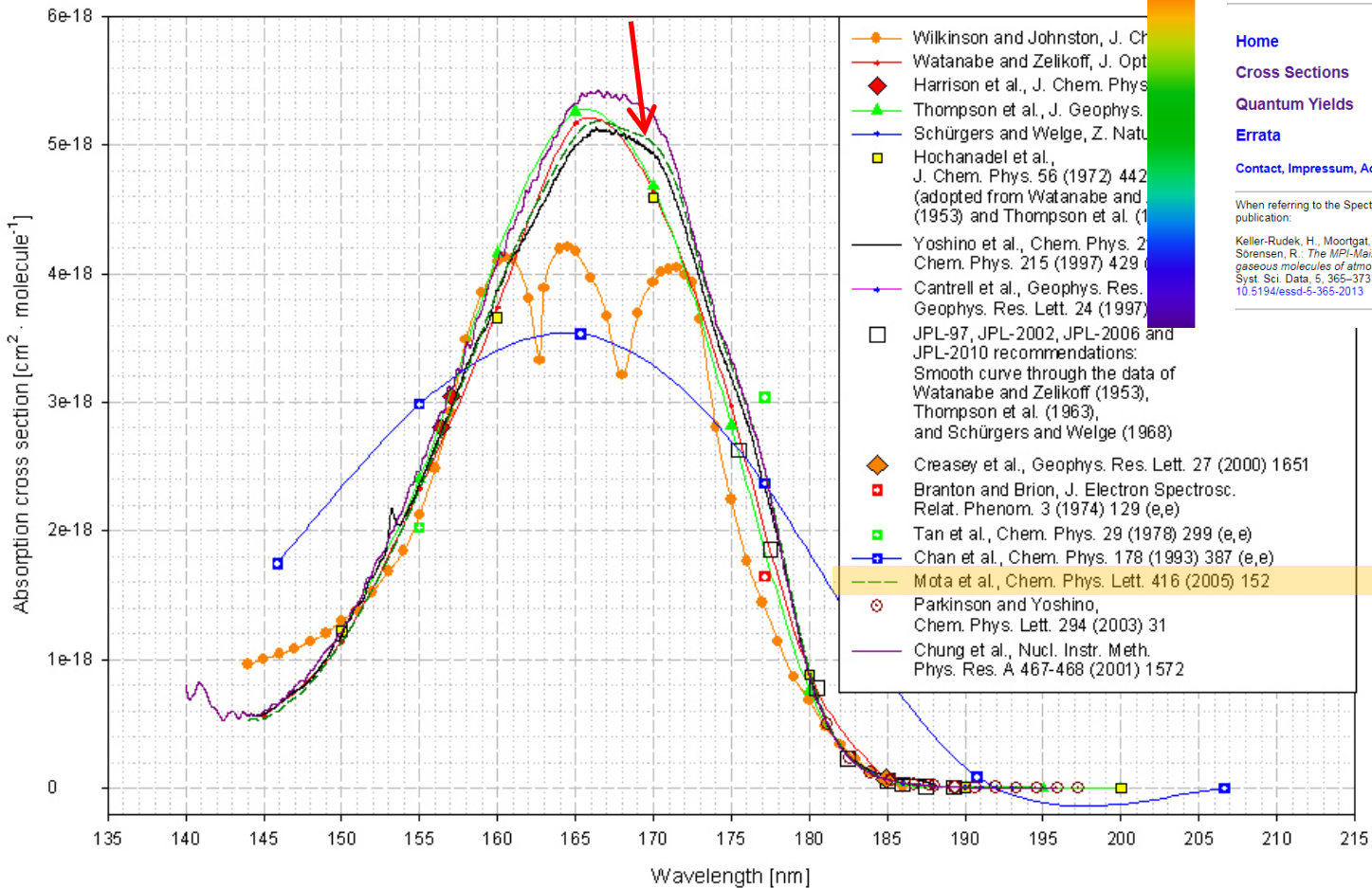


- Follow the nature (“shorter” = “stronger”)
- More than 1 component can be measured at the same time
- No need for high-spectral resolution
- Can be made compact
- No moving parts
- Moderate costs
- Major spare part: D2 UV lamp



- Easy to measure H₂O absorption
- Need for accurate H₂O cross-sections
- Need to have an excellent H₂O generator (primary, traceable)
- Can be calculated (ab initio) – on going 2021+ after R Schinke (90's)

Mota et al (2005)



The MPI-Mainz UV/VIS Spectral Atlas
of Gaseous Molecules of Atmospheric Interest
Hannelore Keller-Rudek¹, Geert K. Moortgat², Rolf Sander², Rüdiger Sörensen¹

Home
Cross Sections
Quantum Yields
Errata
Contact, Impressum, Acknowledgements

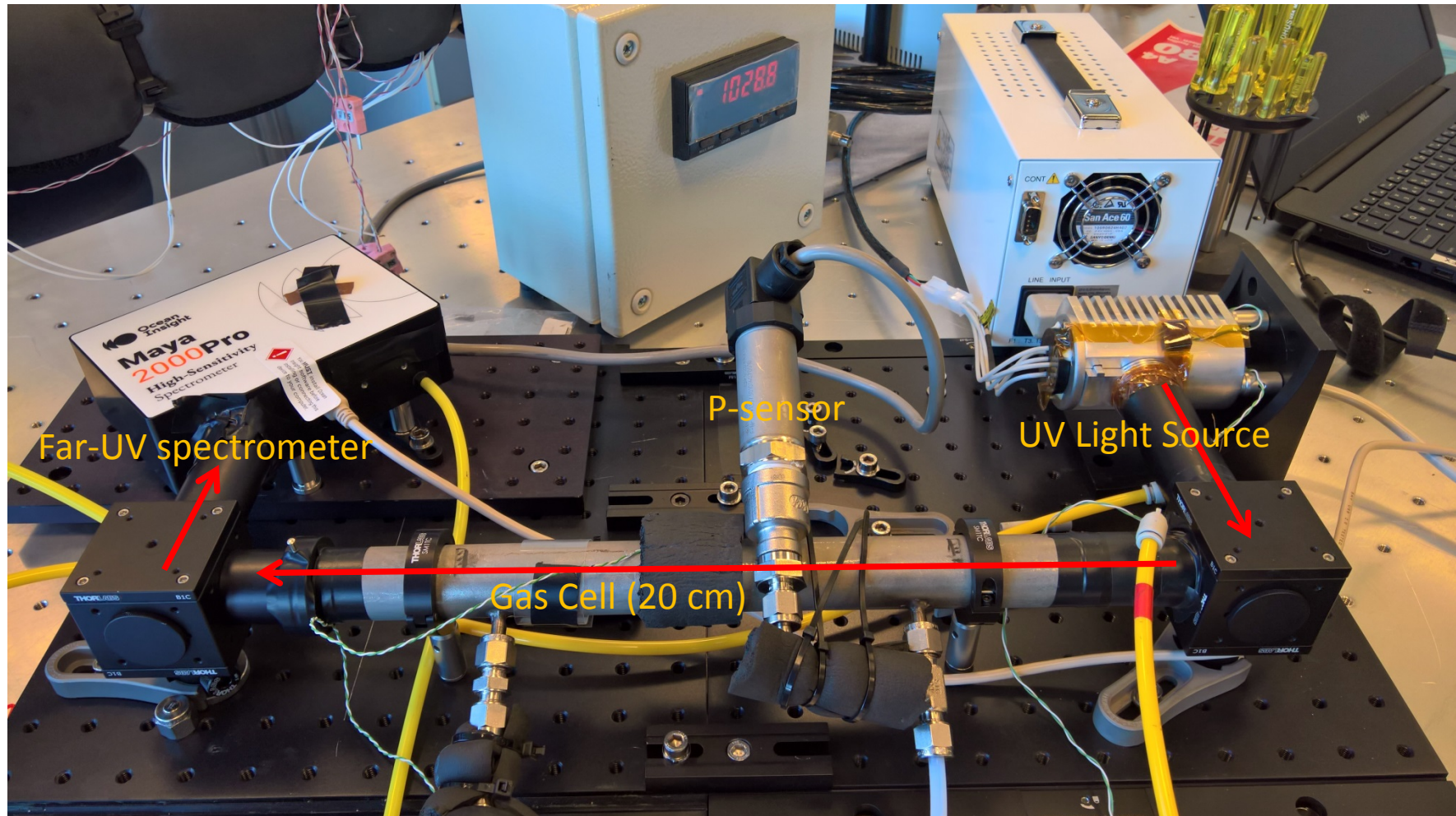
When referring to the Spectral Atlas, please cite our publication:
Keller-Rudek, H., Moortgat, G. K., Sander, R., and Sörensen, R.: *The MPI-Mainz UV/VIS spectral atlas of gaseous molecules of atmospheric interest*, Earth Syst. Sci. Data, 5, 365–373, (2013), DOI: 10.5194/essd-5-365-2013

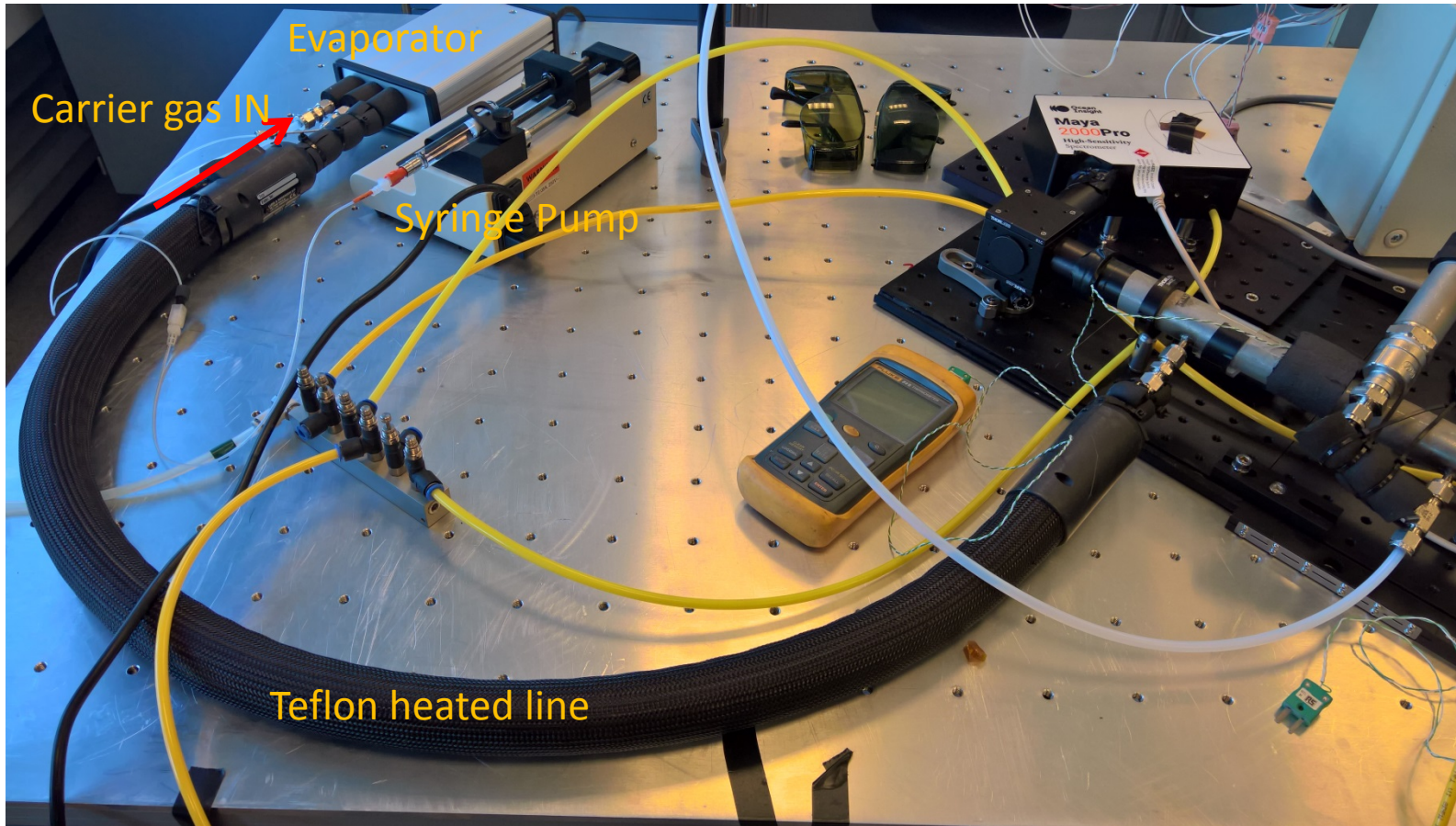
Cross Sections / Hydrogen+water / H₂O / Mota(2005)_298K_114.8-193.9nm

DATAFILE: H2O_Mota(2005)_298K_114.8-193.9nm.txt
NAME: water
FORMULA: H2O
AUTHOR(YEAR): Mota(2005)
T: 298K
λ: 114.8-193.9nm
BIBLIOGRAPHY: R. Mota, R. Parafita, A. Giuliani, M.-J. Hubin-Franskin, J.M.C. Lourenço, G. Garcia, S.V. Hoffmann, M.J. Mason, P.A. Ribeiro, M. Raposo, and P. Limão-Vieira, "Water VUV electronic state spectroscopy by synchrotron radiation", Chem. Phys. Lett. 416, 152-159 (2005); DOI: 10.1016/j.cplett.2005.09.073
COMMENTS: Absorption measurements at a spectral resolution of ~0.075 nm using synchrotron radiation
Absorption cross sections for the 114.80-125.50-nm region at 0.05-nm intervals and for the 125.0-193.9-nm region at 0.1-nm intervals have been obtained by personal communication from Paulo Limão-Vieira (Oct 2005)

Mota et al (2005) as a reference
(absorption measurements at a spectral resolution of ~0.075 nm using synchrotron radiation)

Absorption cross sections of H₂O at room temperature (140-207 nm)





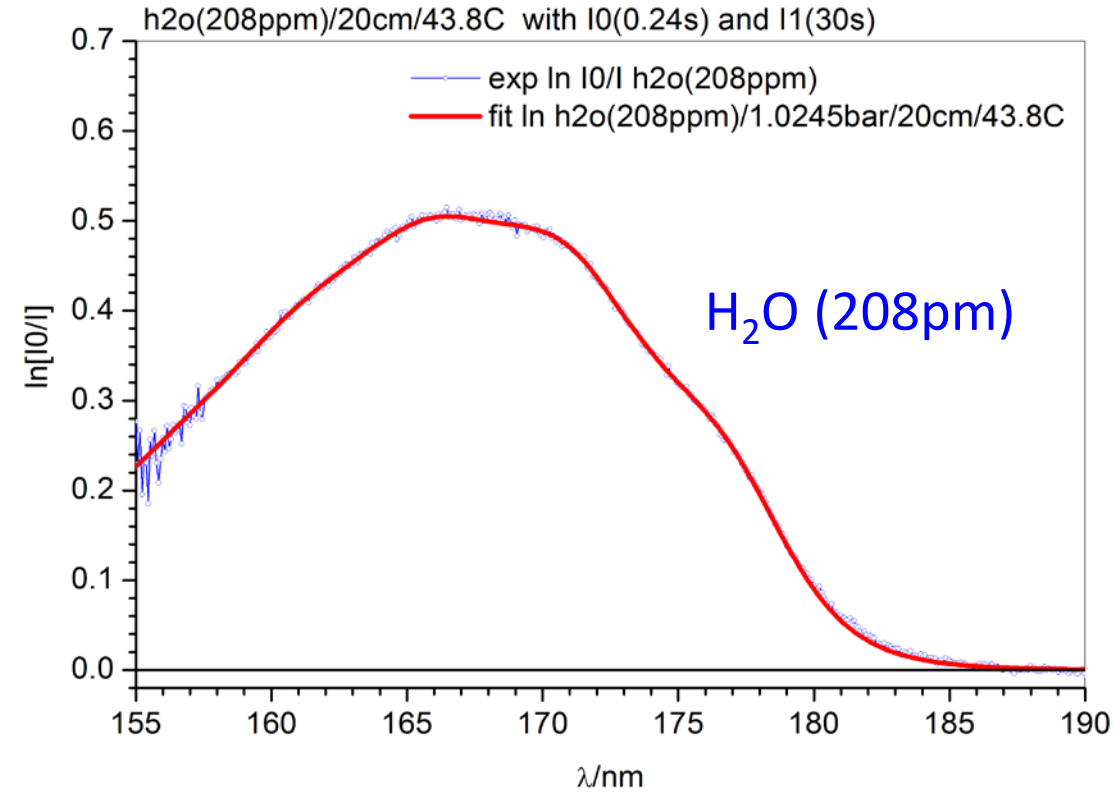
- H₂O vapor generation:
- Single-syringe infusion pump
 - Evaporator
 - Heated Teflon line
 - Dynamic (flow) system

Specifications

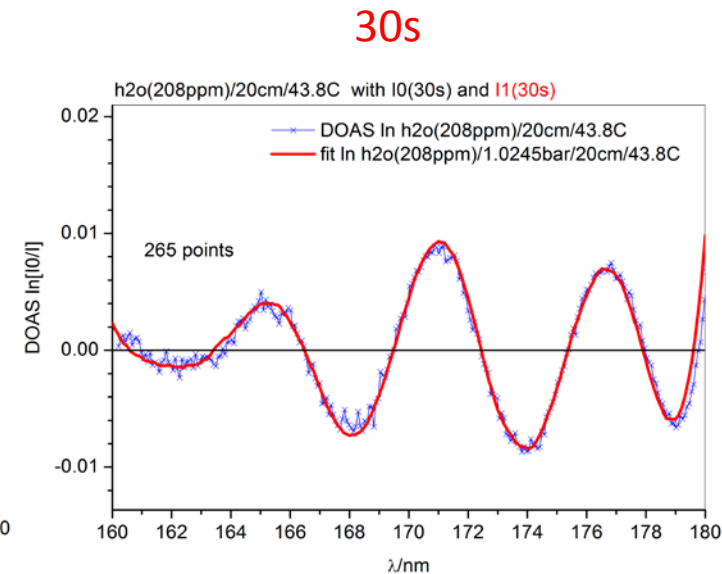
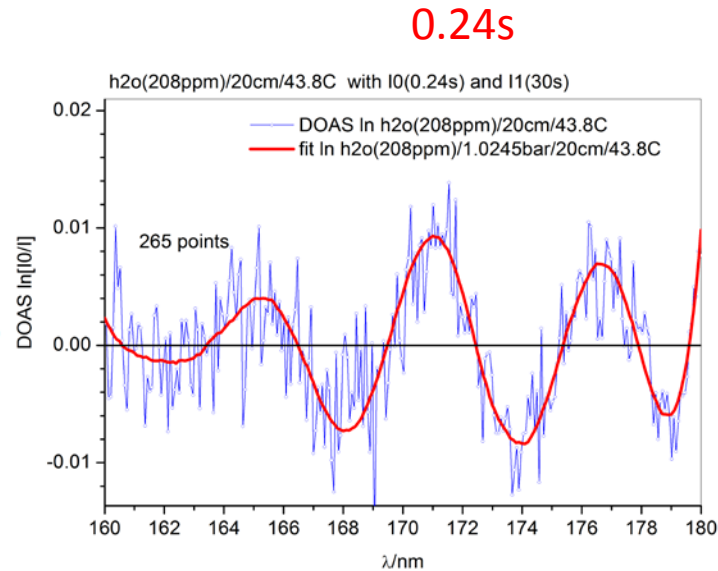
Syringe size accepted	10 µL to 60 mL	
Syringe travel time	9.5 x 10 ⁻⁶ mm/min	
Flow range	w/60 mL syringe	.2 µL/hr to 500 mL/hr
Reproducibility	±.2%	
Linear force	20 lb/sq. in	
Accuracy	±.5%	
Dimensions	9" x 4" x 6"	

Two ways of spectra analysis:

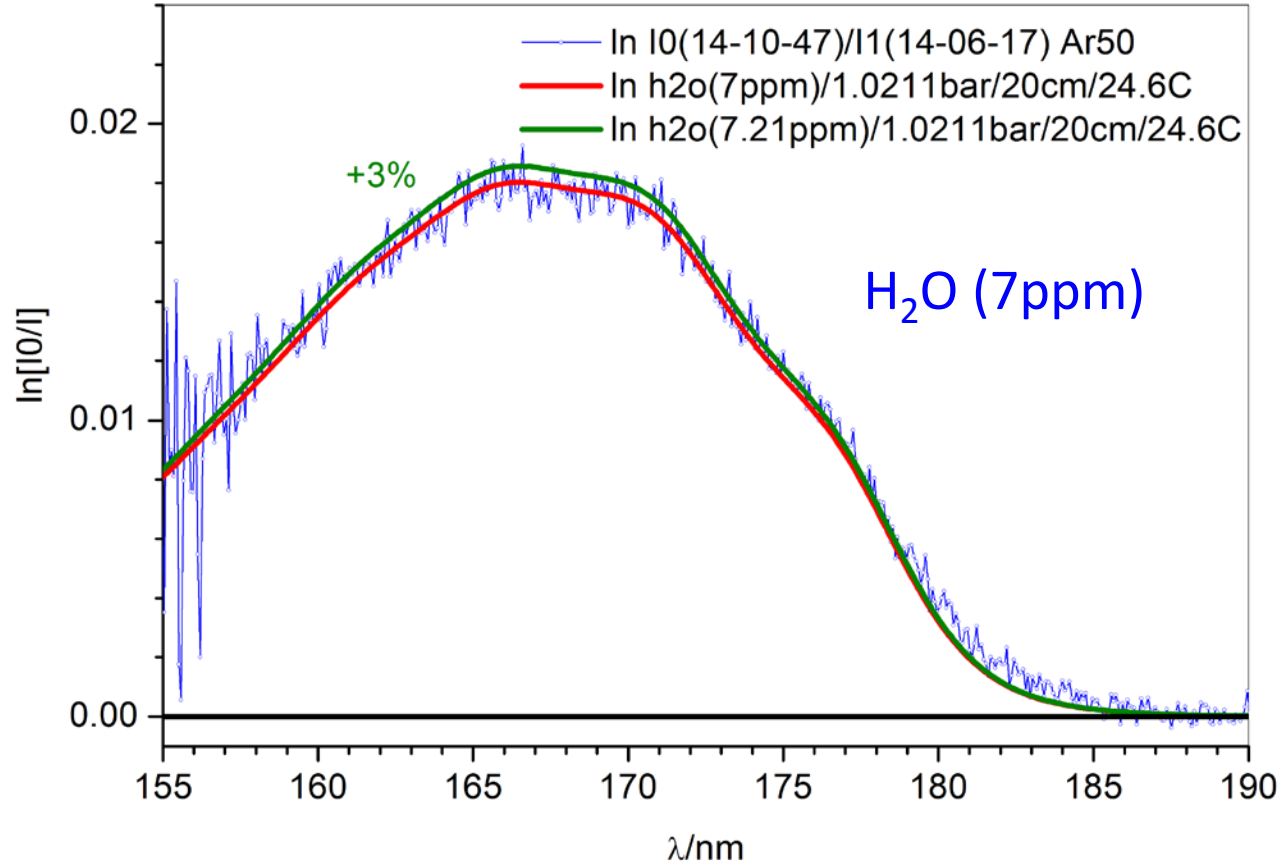
- ❑ On ln-scale (i.e. “normal” spectra analysis): require a good base line, can be effected by interferences with other compounds (e.g. CO₂, O₂)
- ❑ DOAS approach: remove interferences and can be applied for both “fast” and “slow” measurements



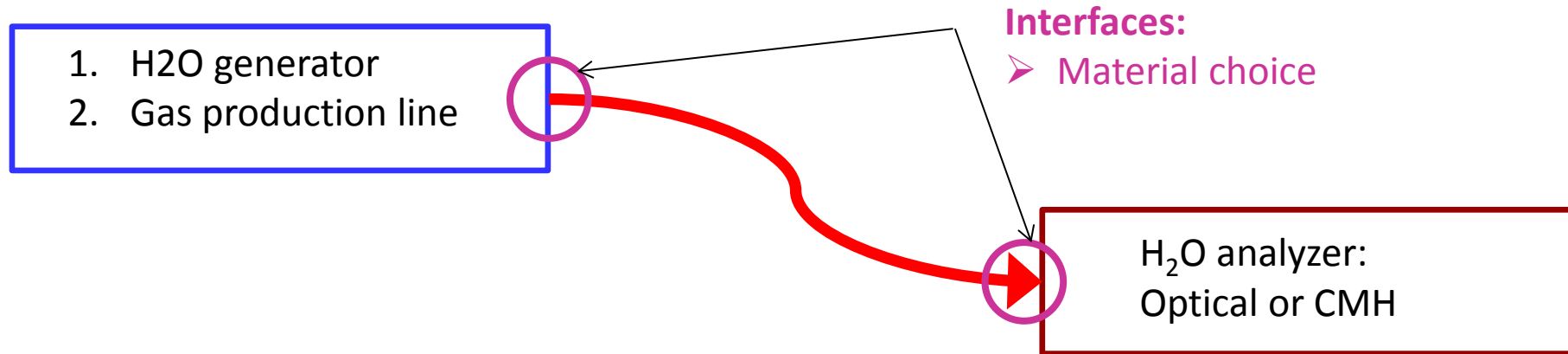
- ❑ Blue: measurements
- ❑ Red: fit with use H₂O cs from Mota et al (2005)



h₂o traces in measurements with Ar with I0(60s) and I1(30s)



- ❑ Chasing H₂O traces in the system with gas supply change for optics (from N₂(5.0) to Ar(5.0)) after measurements with air in the cell
- ❑ +3 % H₂O concentration can clearly been seen in the spectra (at 30 s)
- ❑ 7 ppm x 20 cm = 1.4 ppm x 100 cm
- ❑ To cover ppb scale – pressurize the cell (up to 10 bars)



- 1 m ss electro polished gas cell production
- Pressure range: up to 10 bar
- Temperature: up to 150 °C
- ss electro-polished (heated) gas inlet interface
- Assembling all (with pressure/temperature control)
- Optimization
- Pressure effects on H₂O cross-sections: measurements

A.1.1.3

Improvements in the existing **FTIR-based** trace water measurements in N₂ and Ar

By Seda OĞUZ AYTEKİN

- UME has **Brüker Vertex 70 FT-IR spectrometer**
- In order to upgrade the FT-IR spectrometer for trace water measurements at the ppm-ppb level, two basic components are needed
 - *Gas cell (received on 28.02.2022)*
 - *MCT detector (we are still waiting for it, nevertheless they promised to send the equipment at the end of March 2022 at the latest.)*
- We have ordered these two units even before the start of the Project.
- We still haven't yet receive the necessary equipment from the manufacturers.

- Gas cell has been sent, it is now in our custom Office and we will have it very soon.
- We are planning to finish installing the Gas Cell to FT-IR spectrometer including alignment and performance verification by the end of March.
- Unfortunately we haven't any ideas regarding the delivery time of MCT detector. But we push the company each Monday of each week.



A.1.1.4

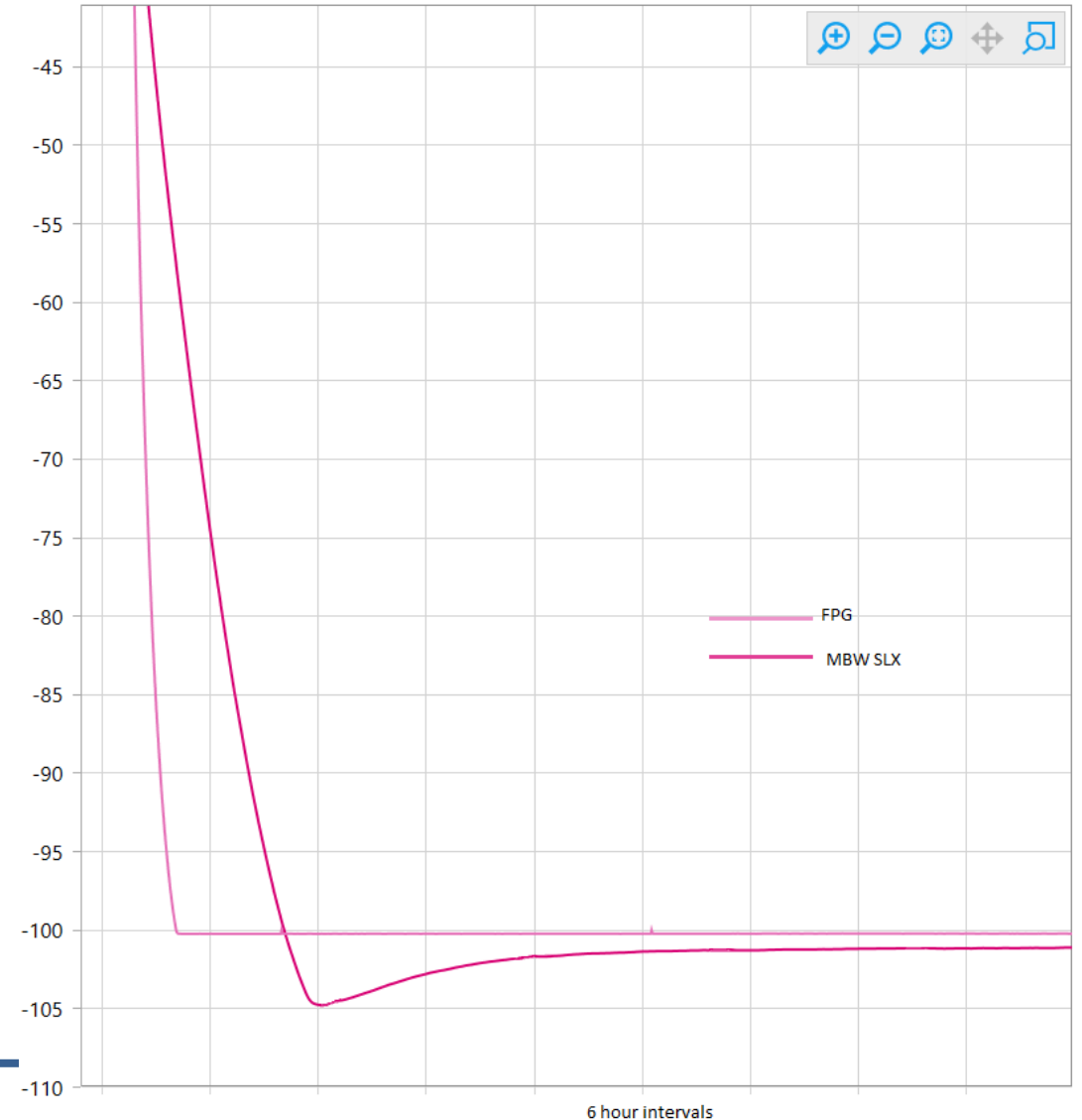
Develop a **NIR** cavity-enhanced frequency-modulated (**CE-FM**) spectroscopy hygrometer

By Ned Hawes



Achievements so far:

- Working transportable frost point generator
- Flow rates 1-5 litre/min on external closed loop
- Generated conditions down to -100°Cfp
- Independent test data down to -90°Cfp



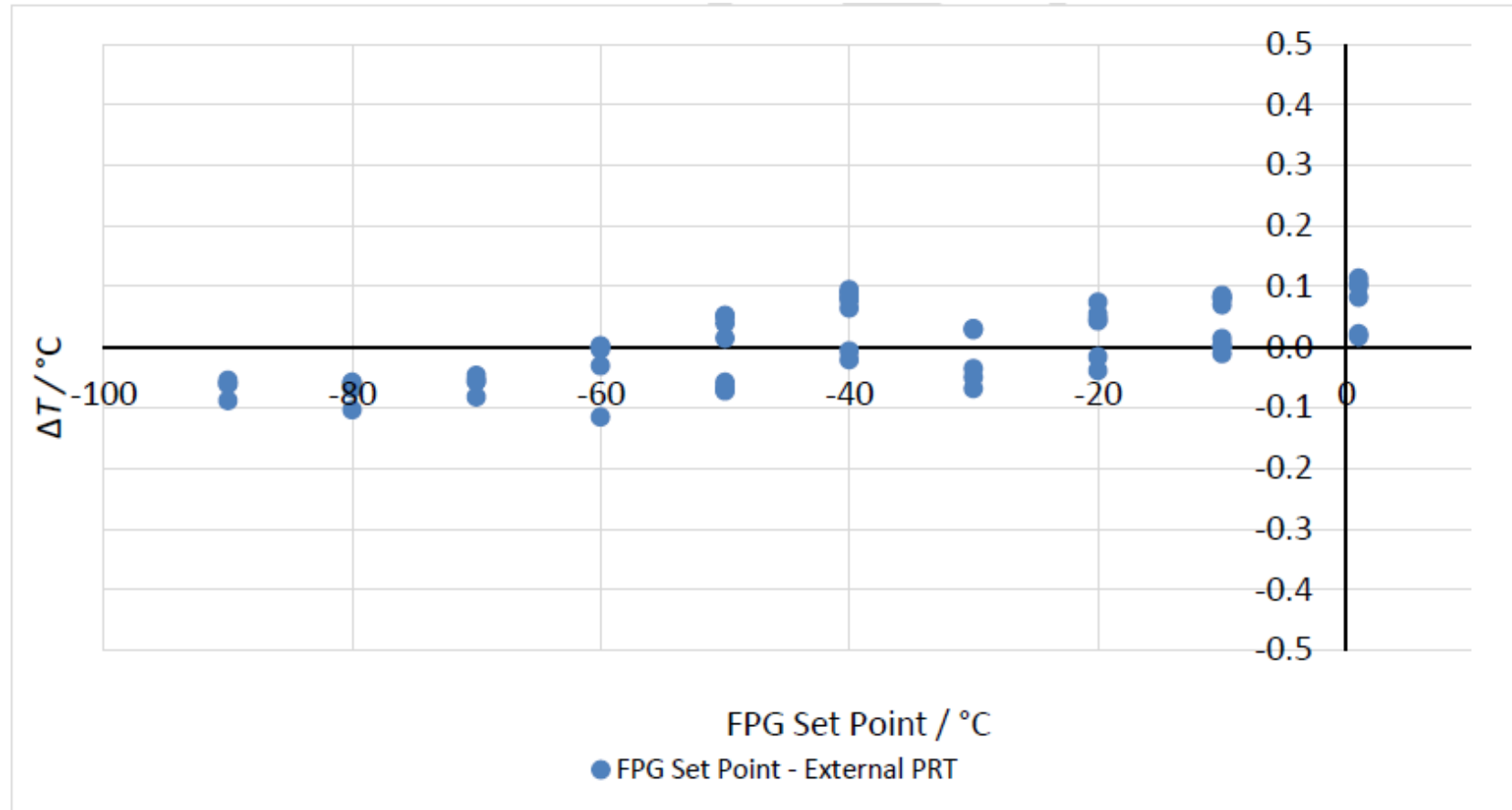


Figure 1: Values of the difference, ΔT , between the FPG Set Point and the External PRT value at each test point between -90 °C and +1 °C.

Reproducibility

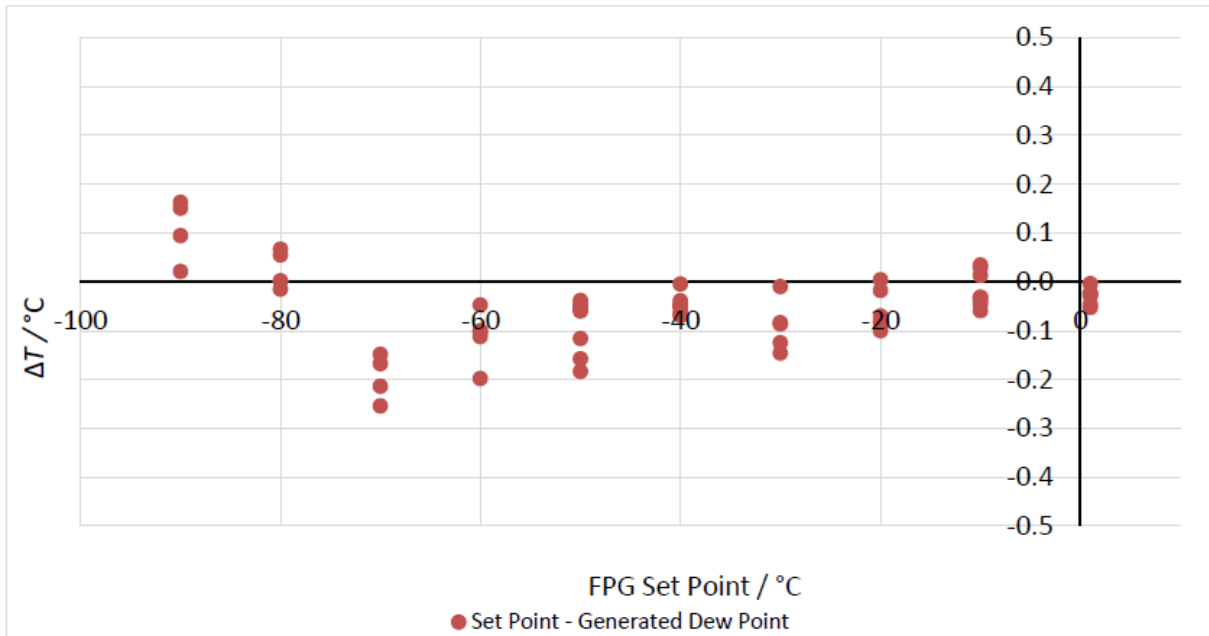
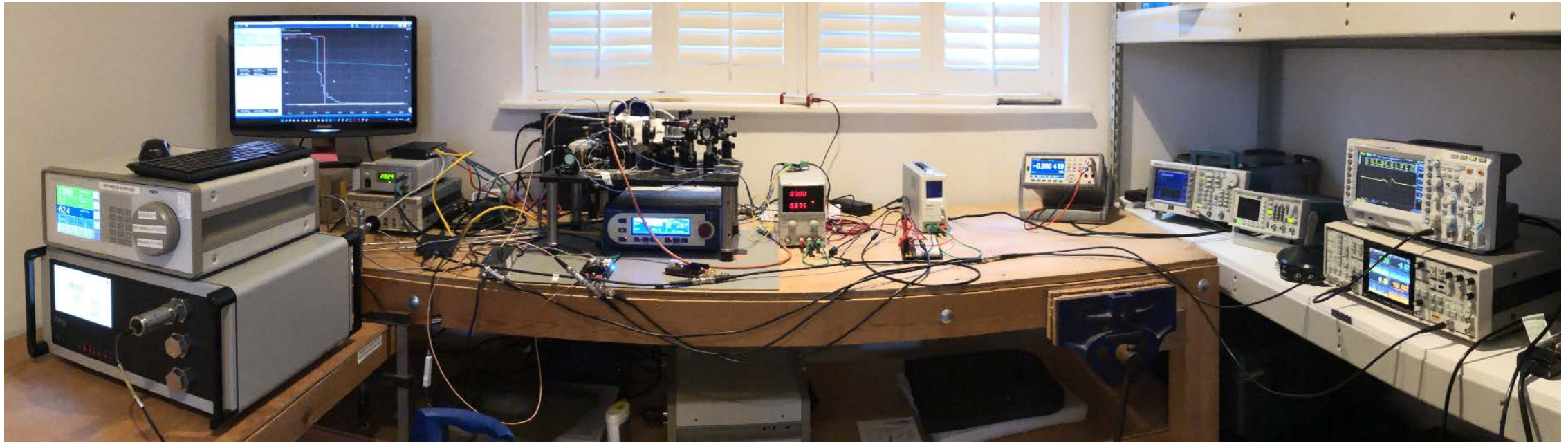


Figure 2: Values of the difference, ΔT , between the FPG Set Point and the Generated dew-point temperature value as measured by a reference chilled-mirror hygrometer at each test point between $-90\text{ }^{\circ}\text{C}$ and $+1\text{ }^{\circ}\text{C}$.

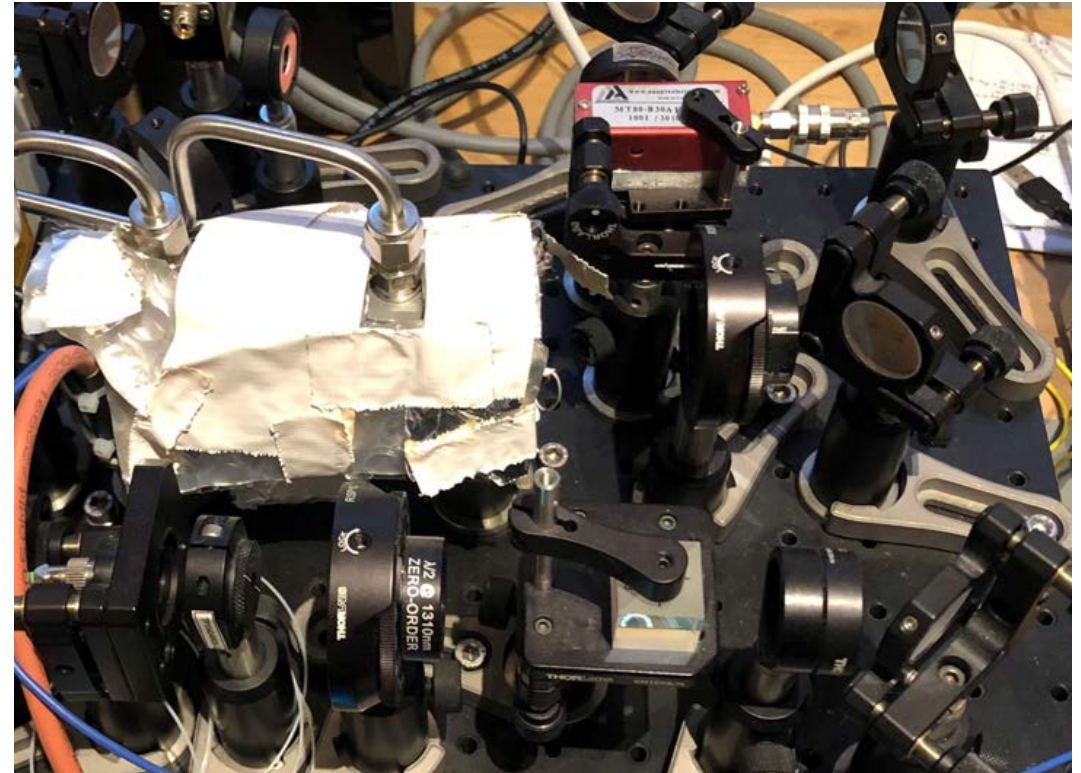
Table 1: Reproducibility estimates across the range $-90\text{ }^{\circ}\text{C}$ and $+1\text{ }^{\circ}\text{C}$ calculated as maximum difference minus minimum difference, based on a total of 57 results with a minimum of 4 results per FPG set point.

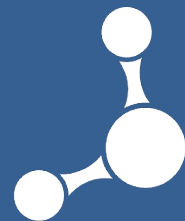
FPG Set Point	Reproducibility Estimate		
	Set point and External PRT	Set Point and Generated Dew Point	Generated Dew Point and External PRT
$^{\circ}\text{C}$	$^{\circ}\text{C}$	$^{\circ}\text{C}$	$^{\circ}\text{C}$
-90	0.03	0.14	0.12
-80	0.05	0.08	0.09
-70	0.04	0.11	0.07
-60	0.12	0.15	0.17
-50	0.12	0.15	0.21
-40	0.12	0.06	0.13
-30	0.10	0.14	0.12
-20	0.11	0.10	0.17
-10	0.10	0.09	0.12
+1	0.10	0.05	0.06



Achievements so far:

- Optical bench set up
- Test cavity constructed and thermally stabilised
- Gas connections
- Laser stabilised and locked to cavity
- **Expected signal profiles achieved**
- Test rig for hygrometric performance using FPG





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Thank you for your attention

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EURAMET

The EMPIR initiative is co-funded by the European Union's Horizon 2020 research and innovation programme and the EMPIR Participating States

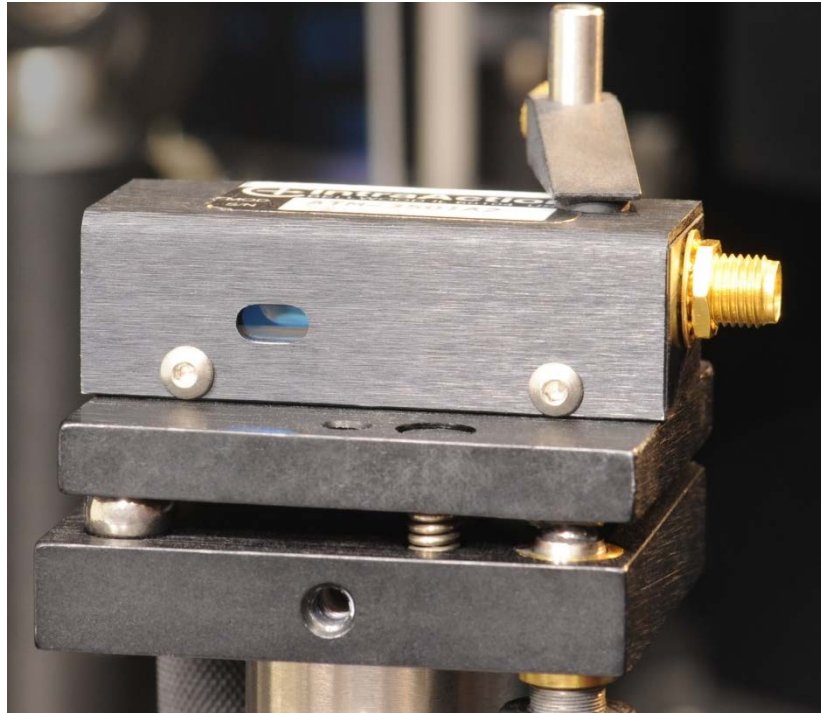


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Extra slides



The EMPIR initiative is co-funded by the European Union's Horizon 2020 research and innovation programme and the EMPIR Participating States

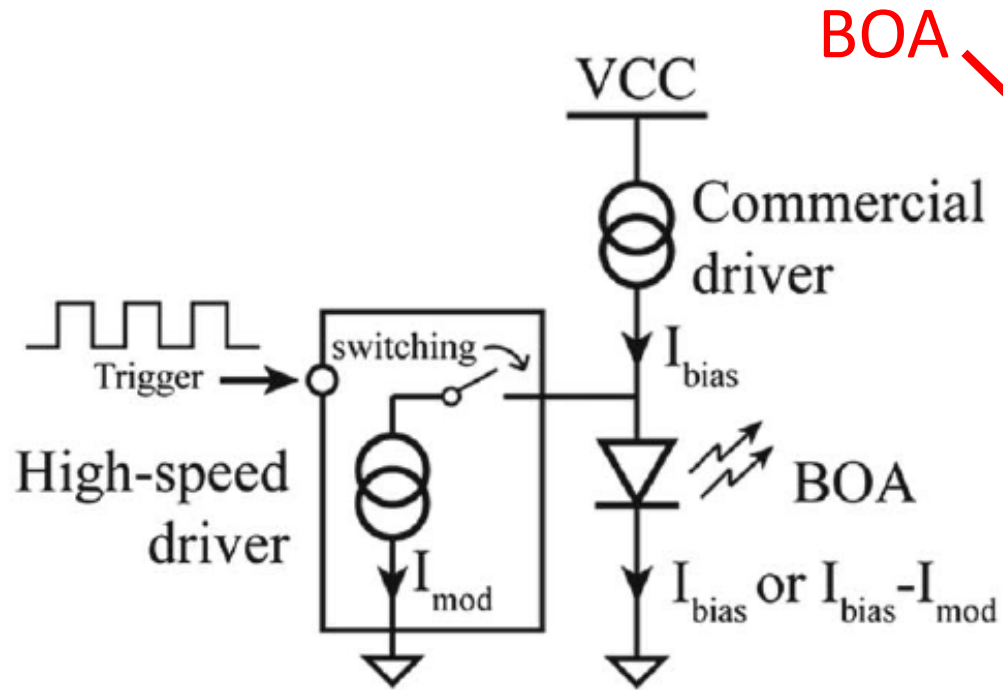


+ 2x

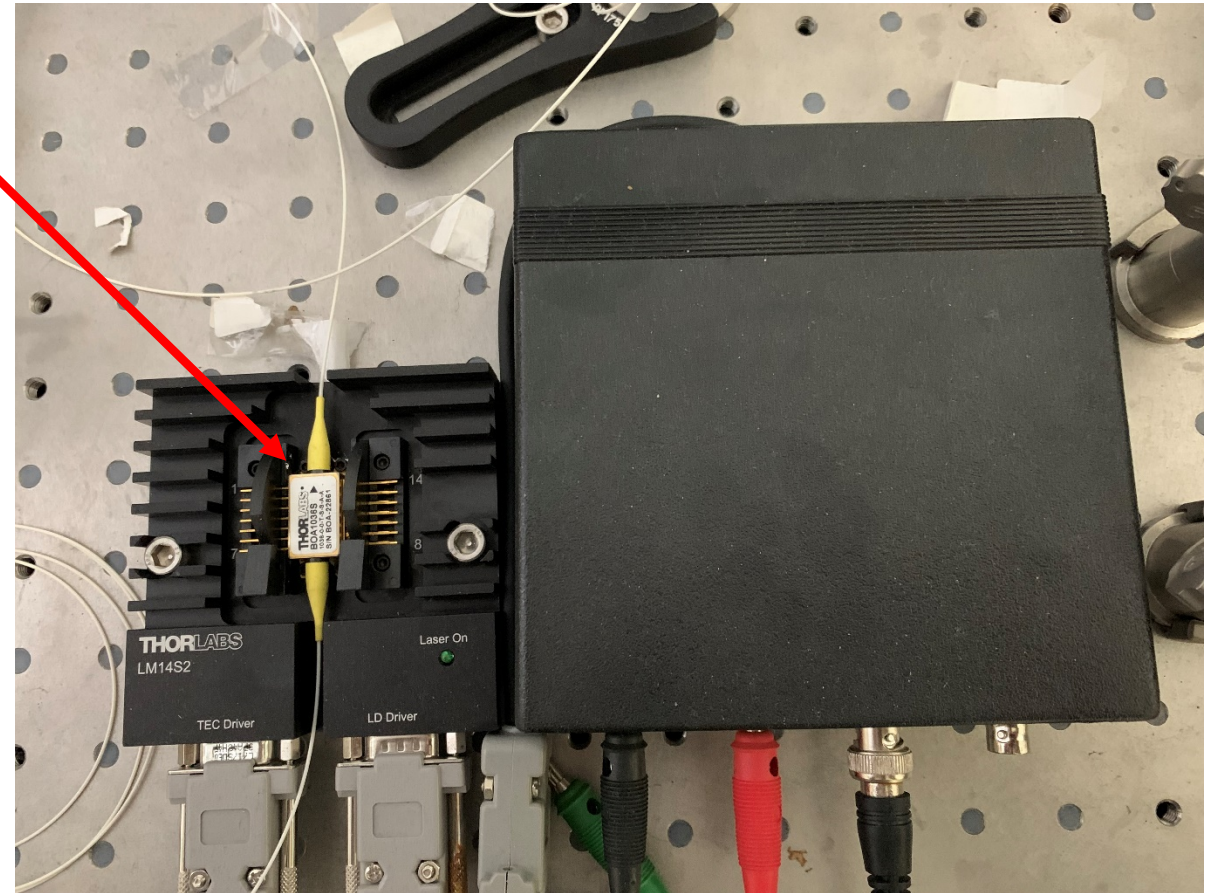


= 90 dB

☺ Reduction of the noise (on τ) caused by a finite extinction ratio of the AOM modulator.



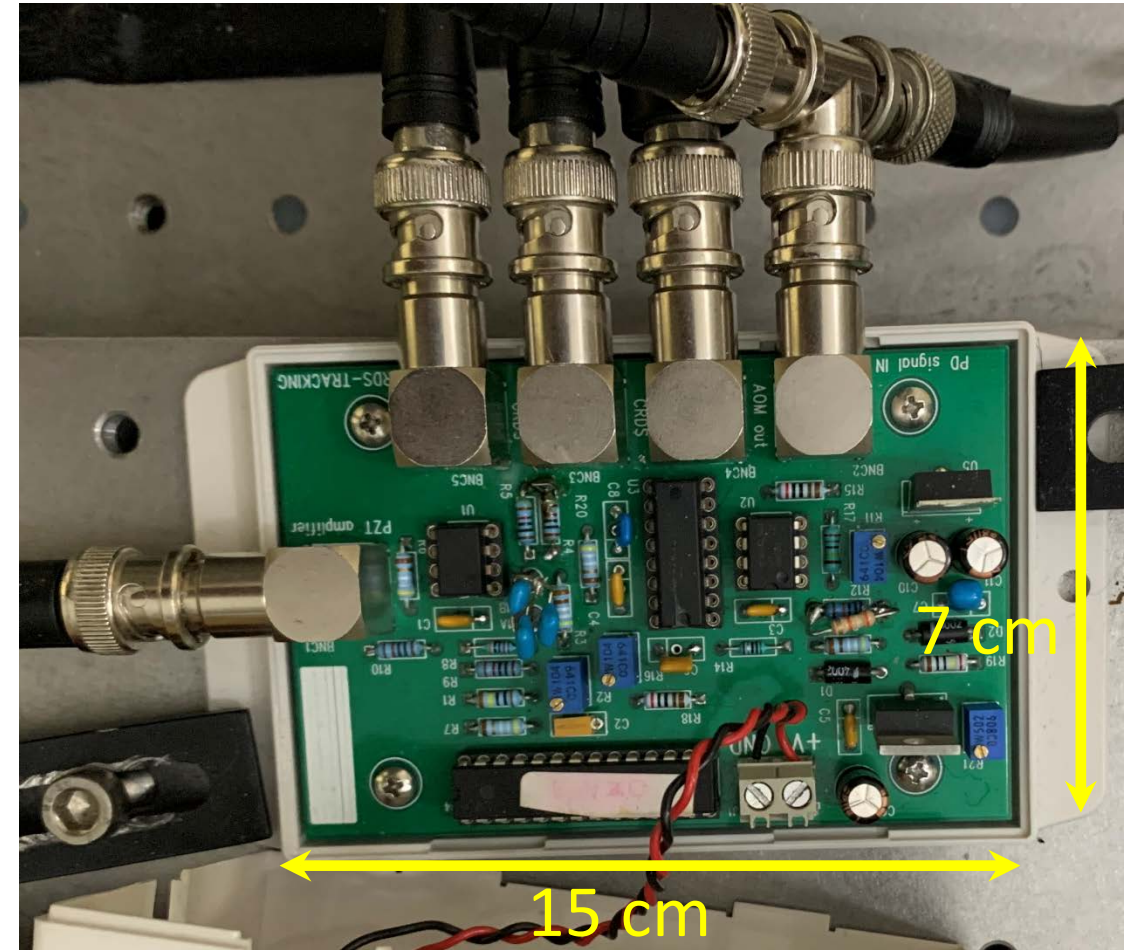
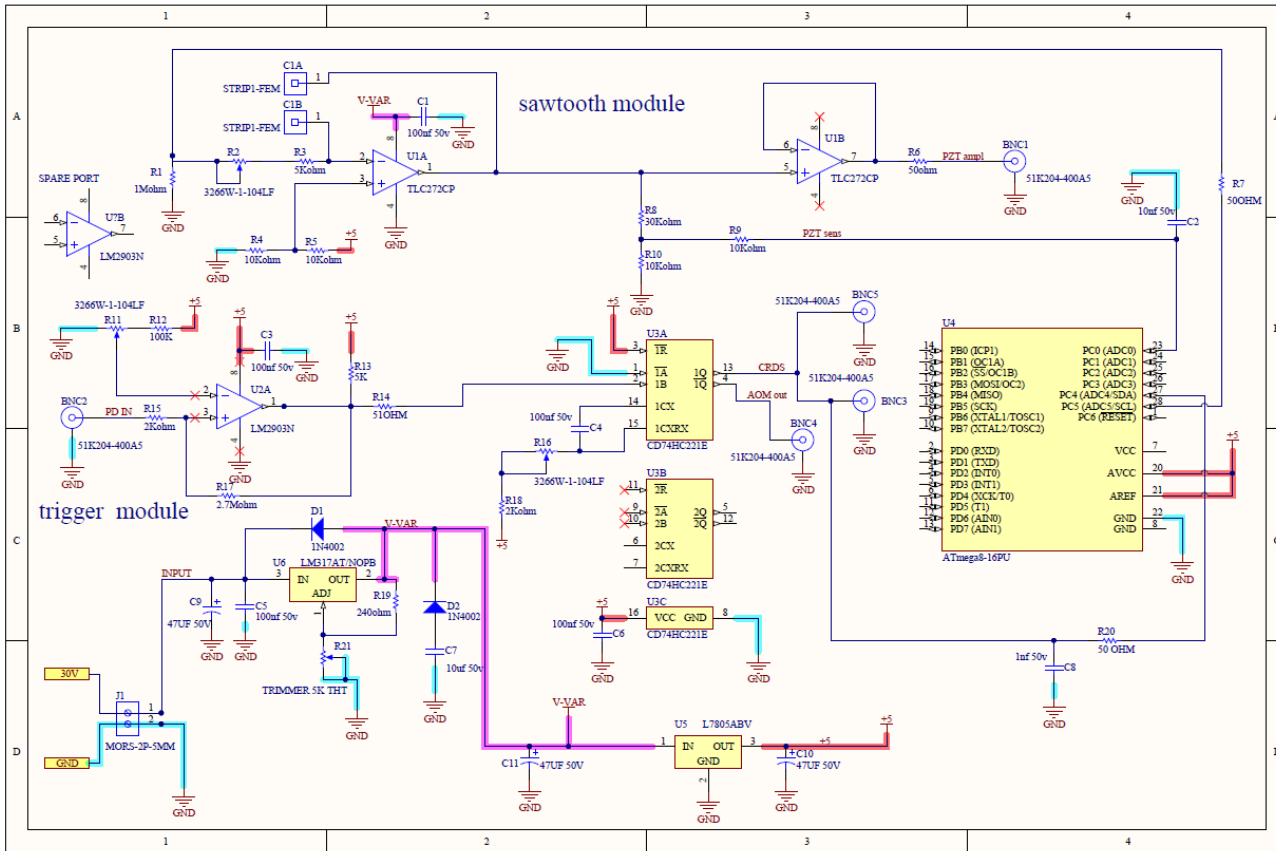
BOA

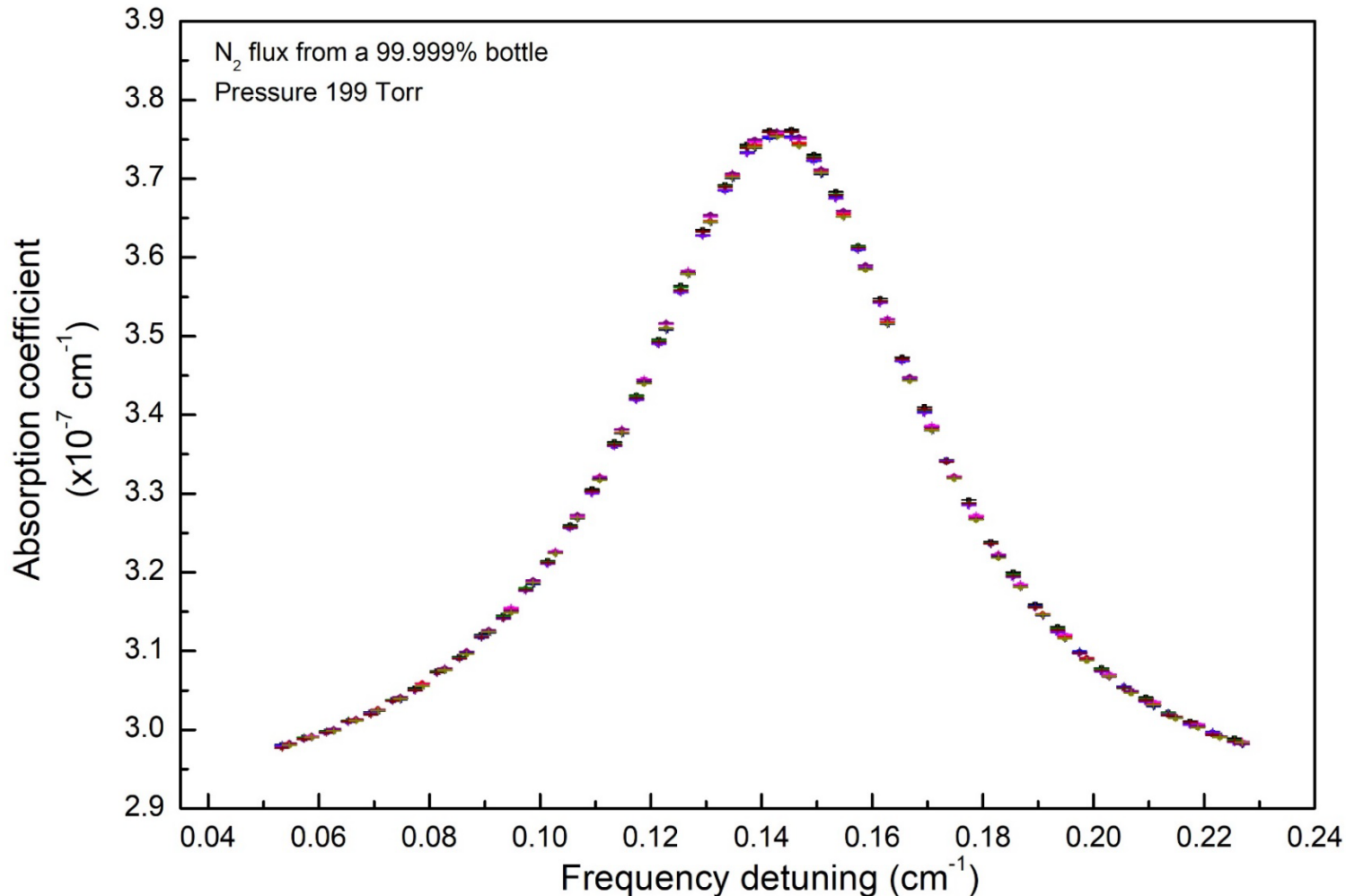


✓ Input power from 500 μ W up to 20 mW;

✓ A further enhancement of the light extinction ratio.

New tracking electronics





Averaging of the spectra are still possible:

😊 reduction of the statistical uncertainty